Subsolidus Phase Relations of the SrO-In2O3-CuO System in Air

Grivel, Jean-Claude; Thydén, Karl Tor Sune

Published in:
Journal of Phase Equilibria and Diffusion

Link to article, DOI:
10.1007/s11669-013-0187-4

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

JPEDAV (2013) 34:89–93
DOI: 10.1007/s11669-013-0187-4
1547-7037 ©ASM International

Subsolidus Phase Relations of the SrO-In_2O_3-CuO System in Air

J.-C. Grivel and K. Thyden

(Submitted June 15, 2012; in revised form November 12, 2012; published online January 24, 2013)

The subsolidus phase relations of the SrO-In_2O_3-CuO system were investigated at 900 °C in air. Under these conditions, five binary oxide phases are stable: Sr_2CuO_3, $SrCuO_2$, $Sr_{14}Cu_{24}O_{41}$, $In_2Cu_2O_5$ and $SrIn_2O_4$. The pseudo-ternary section is characterised by six three-phase regions and is dominated by the $SrIn_2O_4$ phase, which is in equilibrium with all other phases. No Sr equivalents of the $Ca_8In_2Cu_4O_{15}$, $Ca_9In_{14}Cu_2O_{32}$, $Ba_2In_2CuO_6$, $Ba_2InCuO_{4.5}$ or $Ba_3In_4Cu_3O_{12}$ phases were formed.

Keywords CuO, In_2O_3, phase equilibria, SrO, x-ray diffraction

1. Introduction

After the discovery of superconducting compounds with high critical temperature (T_c) in the Tl-Ba-Ca-Cu-O system,[1] attempts have been made to replace thallium by harmless elements, in particular indium, which is located just above Tl in the periodic table. However, as reported by Hur et al.[2] the solubility limit of In in the phase having the highest T_c is limited to about 20 at.% and In actually results in partial suppression of the superconducting properties. In contrast, superconductivity was observed in the In-based cuprates $In_{0.3}Pb_{0.7}Ca_{0.8}Y_{0.2}Sr_2Cu_2O_y$ and $(Bi,In)Sr_2(Gd,Ca)Cu_2O_y$ with T_c values of 60 and 42 K respectively.[3,4] The effect of In substitution in a variety of superconducting cuprates differs significantly depending on the particular compound. In $Bi_2Sr_2Ca_2Cu_3O_{10}$, $HgBa_2CaCu_2O_6$ and $(La,Gd)CaBa_3Cu_7O_z$, In doping is detrimental to the superconducting properties.[5-7] In contrast, in $YBa_2Cu_3O_7$, a small amount of In substitution for Y appears to increase T_c slightly,[8] whereas it can even induce superconductivity in $(Nd,Ce)_2CuO_{4-y}$.[9] Interestingly, superconductivity can be induced by Zn doping in In_2O_3.[10] The synthesis of a layered cuprate with composition reminiscent to that of some superconducting cuprates, i.e. $In_2Ba_2CuO_{6-\delta}$, was also reported[11] but this compound appears to be an insulator.

Whereas the phase equilibria of the pseudo-ternary systems CaO-In_2O_3-CuO and BaO-In_2O_3-CuO have been published,[12,13] we are not aware of reports on the SrO-In_2O_3-CuO system. We have therefore determined the phase equilibria in the latter system in view of the possible occurrence of new ternary oxide phases as well as in order to provide a comparison with related systems.

J.-C. Grivel and **K. Thyden**, Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark. Contact e-mail: jean@dtu.dk

1.1 Previous Work

Under ambient pressure conditions, In_2O_3 crystallises in the *Ia*-3 space group (cubic).[14] Several studies[15-20] have been devoted to the SrO-CuO system, in which three phases are known to be stable at 800 °C in air: Sr_2CuO_3 (orthorhombic, space group *Immm*[21]), $SrCuO_2$ (orthorhombic, space group *Cmcm*[21]) and $Sr_{14}Cu_{24}O_{41}$, which is sometimes described as $Sr_3Cu_5O_8$ (orthorhombic, space group *Fmmm*[22]). Under conditions of lower oxygen partial pressure, an additional binary oxide with $SrCu_2O_2$ composition was observed.[20,23] The $SrCu_2O_3$ and $Sr_2Cu_3O_5$ phases were synthesised under high pressure (1.7-8 GPa).[24]

According to the BaO-In_2O_3-CuO and CaO-In_2O_3-CuO phase equilibrium studies published by Horyń et al.[12] and Godzhieva et al.[13] respectively, in air in the temperature range 900-950 °C, the In_2O_3-CuO pseudo binary system contains only one binary oxide phase: $In_2Cu_2O_5$. The structure of this compound has been refined by Freund and Müller-Buschbaum[25] as orthorhombic (space group $P2_1nb$). In_2CuO_4 single crystals with tetragonal symmetry were grown from a melt consisting of a 0.9BaO:0.1-$KO_{0.5}$:2SrO:4CuO nominal composition by cooling from 1150 to 300 °C.[26] This phase does not appear in the above mentioned equilibrium diagrams.[12,13]

Partial data on the SrO-In_2O_3 system can be found in the In_2O_3-TiO_2-SrO phase diagram section established by Li et al.[27] at 1350 °C in air. Under these conditions, a single binary oxide compound is formed: $SrIn_2O_4$. The structure of this phase (orthorhombic, space group *Pnam*) was reported by von Schenk and Müller-Buschbaum.[28] $Sr_2In_2O_5$ is only stable at higher temperatures.[29]

In the SrO-In_2O_3-CuO system, no ternary oxide phase has been reported so far.

2. Experimental Details

High purity In_2O_3, $SrCO_3$ and CuO powders (all ≥99.9%) were thoroughly mixed in an agate mortar and calcined at 900 °C for 60 h. In total, 36 nominal compositions were

Table 1 Phases observed in selected samples after equilibration and crystallographic data for the majority phases

Nominal cation ratio In:Sr:Cu	Phases (XRD)[a]	Space group[b]	Lattice parameters[c]			
			a, Å	*b*, Å	*c*, Å	β, °
0:0:100	CuO	*C*2/*c*	4.692(10)	3.425(2)	5.124(13)	99.52(3)
1:0:99	CuO ($In_2Cu_2O_5$)	*C*2/*c*	4.694(11)	3.422(2)	5.124(15)	99.54(4)
49:0:51	$In_2Cu_2O_5$ (CuO)	$P2_1nb$	12.291(5)	10.538(4)	3.279(2)	…
50:0:50	$In_2Cu_2O_5$	$P2_1nb$	12.298(4)	10.547(3)	3.281(1)	…
51:0:49	$In_2Cu_2O_5$ (In_2O_3)	$P2_1nb$	12.296(3)	10.538(3)	3.279(1)	…
50:1:49	$In_2Cu_2O_5$ (In_2O_3, $SrIn_2O_4$)	$P2_1nb$	12.307(7)	10.549(5)	3.280(2)	…
49:1:50	$In_2Cu_2O_5$ (CuO, $SrIn_2O_4$)	$P2_1nb$	12.306(7)	10.552(5)	3.282(2)	…
99:1:0	In_2O_3 ($SrIn_2O_4$)	*Ia*-3	10.117(4)	…	…	…
100:0:0	In_2O_3	*Ia*-3	10.118(3)	…	…	…
99:0:1	In_2O_3 ($In_2Cu_2O_5$)[d]	*Ia*-3	10.114(3)	…	…	…
98:0:2	In_2O_3 ($In_2Cu_2O_5$)	*Ia*-3	10.121(3)	…	…	…
68:32:0	$SrIn_2O_4$ (In_2O_3)	*Pnam*	9.842(5)	11.494(4)	3.261(3)	…
2/3:1/3:0	$SrIn_2O_4$	*Pnam*	9.833(3)	11.491(2)	3.265(1)	…
66:34:0	$SrIn_2O_4$ (SrO)	*Pnam*	9.839(4)	11.490(4)	3.264(2)	…
65.67:33.33:1	$SrIn_2O_4$ ($Sr_{14}Cu_{24}O_{41}$)	*Pnam*	9.834(4)	11.499(3)	3.264(2)	…
66.67:32.33:1	$SrIn_2O_4$ (In_2O_3, $In_2Cu_2O_5$)	*Pnam*	9.832(5)	11.494(5)	3.263(3)	…
1.00:66.67:32.33	Sr_2CuO_3 ($SrIn_2O_4$, SrO)	*Immm*	12.701(1)	3.912(1)	3.499(1)	…
0.00:66.67:33.33	Sr_2CuO_3	*Immm*	12.704(1)	3.913(1)	3.500(1)	…
1.00:65.67:33.33	Sr_2CuO_3 ($SrIn_2O_4$, $SrCuO_2$)	*Immm*	12.701(1)	3.912(1)	3.499(1)	…
1:50:49	$SrCuO_2$ ($SrIn_2O_4$, Sr_2CuO_3)	*Cmcm*	3.572(1)	16.328(3)	3.913(2)	…
0:50:50	$SrCuO_2$	*Cmcm*	3.572(1)	16.325(2)	3.914(2)	…
1:49:50	$SrCuO_2$ ($SrIn_2O_4$, $Sr_{14}Cu_{24}O_{41}$)	*Cmcm*	3.571(1)	16.322(2)	3.912(2)	…
0.5:14.0:23.5	$Sr_{14}Cu_{24}O_{41}$ ($SrIn_2O_4$, $SrCuO_2$)	*Cccm*	11.464(3)	13.400(1)	27.64(1)	…
0.0:14.0:24.0	$Sr_{14}Cu_{24}O_{41}$	*Cccm*	11.465(8)	13.401(3)	27.64(2)	…
0.5:13.5:24.0	$Sr_{14}Cu_{24}O_{41}$ (CuO, $SrIn_2O_4$)	*Cccm*	11.473(6)	13.405(3)	27.62(2)	…

[a]Phases between brackets are minority phases
[b]Space group of the majority phase
[c]The lattice parameters are those of the majority phase
[d]Detected by SEM/EDX but not by XRD

studied. After grinding, pellets were pressed under a pressure of 1.8 kbar and sintered at 900 °C for 60 h. Additional heat treatments under similar conditions with intermediate grinding and pressing were performed until equilibrium was reached. The samples were air-quenched at the end of the sintering treatments. All heat treatments were performed in air.

The phase content of the pellets was checked after each heat treatment by x-ray diffraction (XRD) in a STOE diffractometer using Cu-K_α radiation. Equilibrium was considered as achieved if no differences were detectable in the XRD patterns collected after two consecutive sintering treatments. Silicon powder was added as an internal standard for lattice parameter determinations in selected samples using the UnitCell leastsquares refinement programme.[30] Scanning electron microscopy (SEM) and local compositional analysis were performed in a TM3000 Tabletop Microscope from HITACHI equipped with a QUANTAX 70 EDS analysis system.

3. Results and Discussion

3.1 SrO-CuO

Three binary oxide phases were formed at 900 °C in air: Sr_2CuO_3, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{41}$, in agreement with previous reports.[15-20] The $SrCu_2O_2$ phase was not found in the present study as a consequence of the lack of stability of this phase in air.[20,23] The high-pressure phases $SrCu_2O_3$ and $Sr_2Cu_3O_5$[24] were not formed either.

3.2 In_2O_3-CuO

In agreement with the results presented in Ref 12 and 13, $In_2Cu_2O_5$ is the only binary oxide phase stable at 900 °C in air in this system. The detection of $In_2Cu_2O_5$ in the sample with $Cu_{0.99}In_{0.01}$ nominal cation composition, coupled with the similar lattice parameters for CuO in this sample and in

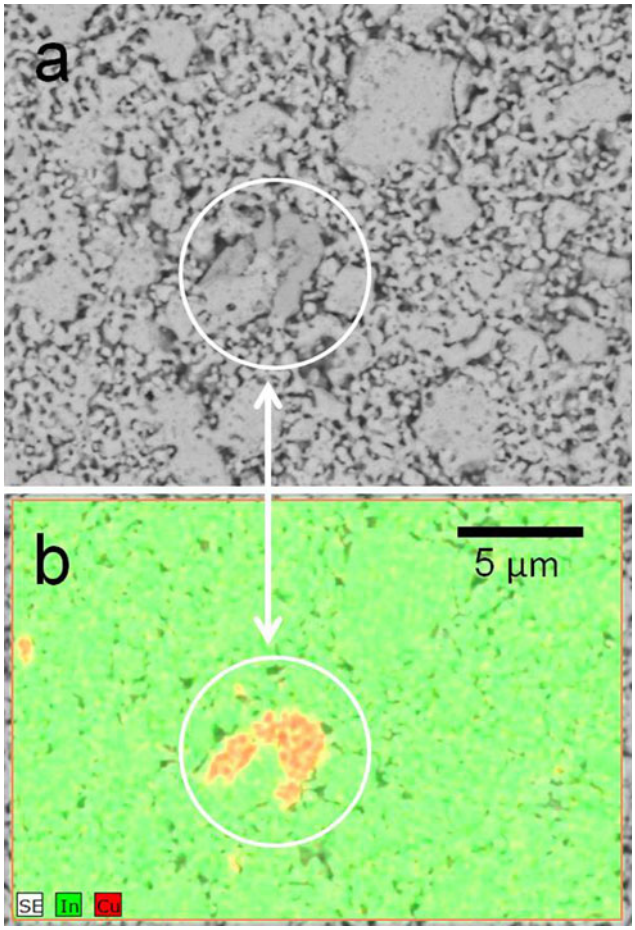

Fig. 1 SEM pictures [(a) backscattering mode and (b) EDS elemental map] showing evidence for coexistence of $In_2Cu_2O_5$ and In_2O_3 in the sample with $In_{0.99}Cu_{0.01}O_y$ nominal composition. The black areas are due to porosity. The encircled particle has an In:Cu atomic ratio of 53 ± 3:47 ± 3

the pure CuO sample (Table 1) allow concluding that no extended substitution of In occurs in CuO under the present experimental conditions. The situation of the In_2O_3 rich part of the system is more intricate. In the works of Horyń et al.[12] and Godzhieva et al.,[13] no solid state solubility of Cu in In_2O_3 was reported. However, according to a recent report by Li et al.,[31] 1 at.% Cu can be introduced in In_2O_3. Using $InCl_3$ and $CuCl_2$ presursors and annealing at 900 °C in pure O_2, Sasaki et al.[32] even claim that single phase samples are obtained for a nominal composition described as In_2O_3:Cu. In the present study, $In_2Cu_2O_5$ impurities are detected by XRD only in samples with $x \geq 0.02$ in $In_{1-x}Cu_xO_y$ nominal compositions, whereas the sample with overall stoichiometry corresponding to a In:Cu = 99:1 atomic ratio appears to be single phase. However, the lattice parameter of the In_2O_3 phase is not affected within the accuracy limit of our measurements. Due to the limited resolution of x-ray diffraction, microscopical observations were performed on the "$In_{0.99}Cu_{0.01}O_y$" sample. As shown in Fig. 1, particles characterised by a slightly darker contrast in backscattering mode are present in the sample. EDS

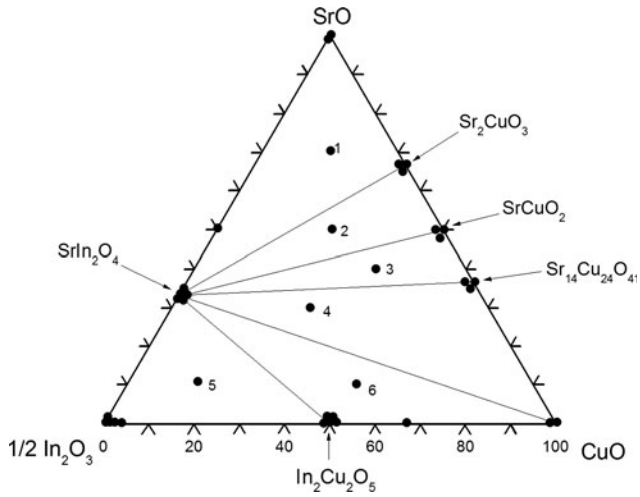

Fig. 2 Phase equilibria of the SrO-In_2O_3-CuO system at 900 °C in air. Dots represent the studied compositions. The numbers 1-6 refer to the XRD patterns that are shown in Fig. 3

analysis on particles with sizes larger than 1 µm consistently yield an In:Cu atomic ratio close to that corresponding to $In_2Cu_2O_5$ (In:Cu = 53 ± 3:47 ± 3) . These particles are dispersed in an In_2O_3 matrix. We therefore conclude that Cu substitution in In_2O_3 must be limited to a value significantly lower than 1 at.% under the present experimental conditions, in agreement with the data published in Ref 12 and 13. As for the $In_2Cu_2O_5$ phase, it appears to be stoichiometric as deviations from the ideal composition result in equilibrium with either In_2O_3 (In excess) or CuO (Cu excess) as detailed in Table 1.

3.3 In_2O_3-SrO

In this pseudo-binary system, $SrIn_2O_4$ is the only binary oxide phase stable under the present conditions.

Due to the strong tendency of SrO to form $Sr(OH)_2 \cdot H_2O$ upon contact with air, we could not perform accurate lattice parameter determinations in the SrO-rich part of the diagram. However, the clear presence of $SrIn_2O_4$ as inferred by XRD analysis in the sample with $Sr_{0.99}In_{0.01}O_x$ nominal composition, suggests that the solubility of In in SrO is rather low as previously published,[27] however at a significantly higher temperature (1350 °C). There is no evidence for Sr substitution in In_2O_3, as $SrIn_2O_4$ is detected in a sample with $In_{0.99}Sr_{0.01}O_y$ nominal composition and the lattice parameters of In_2O_3 are not affected by the presence of Sr (Table 1). Likewise, the $SrIn_2O_4$ phase appears to be stoichiometric.

3.4 SrO-In_2O_3-CuO

The subsolidus tie-line compatibilities of phases in the pseudo-ternary SrO-In_2O_3-CuO phase diagram in air at 900 °C are shown in Fig. 2. There are five binary oxide phases: Sr_2CuO_3, $SrCuO_2$, $Sr_{14}Cu_{24}O_{41}$, $In_2Cu_2O_5$ and $SrIn_2O_4$ but no ternary oxide phases. All of the six three-phase regions are in contact with the $SrIn_2O_4$ phase, which can thus be in equilibrium with any of the other compounds

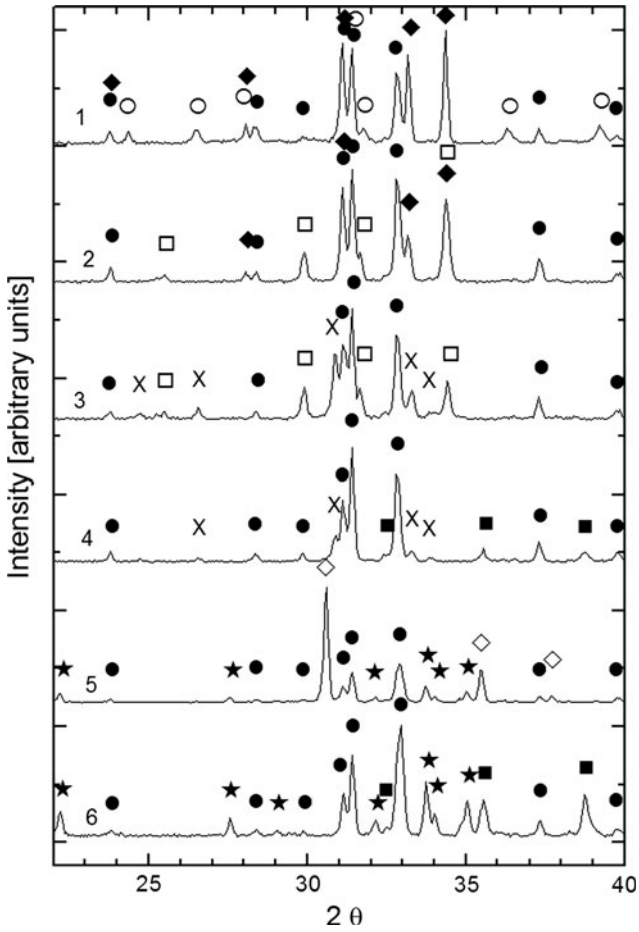

Fig. 3 Representative XRD patterns collected on samples with compositions lying in each of the three-phase regions of the pseudo-ternary sections. The pattern numbers refer to Fig. 2. Phases: ● $SrIn_2O_4$, ○ $Sr(OH)_2{\cdot}H_2O$, ♦ Sr_2CuO_3, □ $SrCuO_2$, X $Sr_{14}Cu_{24}O_{41}$, ■ CuO, ◇ In_2O_3 and ∗ $In_2Cu_2O_5$

depending on the overall composition. Representative XRD patterns for nominal compositions situated in all three-phase regions are shown in Fig. 3. None of the binary oxide phases of the pseudo-binary systems appear to give rise to ternary solid solutions as can be deduced from the appearance of 2-phase or 3-phase equilibria when attempts were made to dope these compounds with the element of the opposite corner (Table 1). The structure of this ternary section is similar to that of the SrO-RE_2O_3-CuO systems where RE = Sc, Y, Lu, Yb, Tm and Er.[33-37] A general trend of the SrO-Ln_2O_3-CuO (Ln = lanthanide) is that the solubility of the lanthanide element in the $Sr_{14}Cu_{24}O_{41}$ phase decreases as the Ln^{3+} ion radius decreases.[38] The radius of the In^{3+} ion is smaller than that of Lu^{3+}.[39] It is therefore not surprising that no In solid solubility is observed in $Sr_{14}Cu_{24}O_{41}$.

4. Conclusion

In air, at 900 °C, the SrO-In_2O_3-CuO system contains six three-phase regions and five binary oxide phases (Sr_2CuO_3, $SrCuO_2$, $Sr_{14}Cu_{24}O_{41}$, $In_2Cu_2O_5$ and $SrIn_2O_4$). No ternary oxide phases were formed under the present equilibration conditions. The structure of this ternary section is similar to that of the SrO-RE_2O_3-CuO systems where RE = Sc, Y, Lu, Yb, Tm and Er, but without $Sr_{14}Cu_{24}O_{41}$-based solid solution.

Acknowledgments

This work was financed by the Danish Ministry of Science, Technology and Innovation.

References

1. Z.Z. Sheng and A.M. Hermann, Bulk Superconductivity at 120 K in the Tl-Ca/Ba-Cu-O System, *Nature*, 1988, **332**, p 138-139
2. N.H. Hur, M. Paranthaman, J.R. Thompson, and D.K. Christen, Superconductivity in the Indium-Doped Tl-1223 Phase: $(Tl_{0.8}In_{0.2})(Sr_{0.8}Ba_{0.2})_2Ca_2Cu_3O_{9-\delta}$, *Physica C*, 1996, **268**, p 266-270
3. R.S. Liu, P.T. Wu, S.F. Wu, W.N. Wang, and P.P. Edwards, First Example of Indium as a Practical Alternative to Thallium in High-T_c Superconductors, *Physica C*, 1990, **165**, p 111-114
4. G. Cao, Y. Qian, W. Yu, S. Wang, Z. Chen, Y. Huang, and Y. Zhang, Synthesis and Characterization of New Cuprates with a (Bi,In)O Monolayer: $(Bi,In)Sr_2(Gd,Ca)Cu_2O_y$, *Physica C*, 1994, **221**, p 278-282
5. C.V. Tomy, R. Prasad, N.C. Soni, K. Adhikary, A. Gulnar, and S.K. Malik, Effect of Sb, Sn and In Doping on the Superconductivity in Bi-Pb-Sr-Ca-Cu-O System, *Solid State Commun.*, 1990, **74**, p 493-496
6. J.Q. Li, C.C. Lam, J. Feng, and K.C. Hung, Effects of In doping in $Hg_{1-x}In_xBa_2CaCu_2O_{6+\delta}$, *Supercond. Sci. Technol.*, 1998, **11**, p 217-222
7. R. Vij, D.C. Kundaliya, A.G. Joshi, D.G. Kuberkar, and R.G. Kulkarni, Suppression of Superconductivity in the $(La_{2.5-x}Gd_{0.5+x})CaBa_{3-x}Sr_x(Cu_{1-y}In_y)_7O_z$ System due to Hole Filling by In and Its Revival by Hole Doping with Ca, *Physica C*, 2002, **371**, p 315-320
8. A.K. Bhattacharya and K.K. Singh, High-Temperature Superconducting Properties in the $Y_{1-x}A_xBa_2Cu_3O_{7-\delta}$ System (A = In, Tl), *Physica C*, 1988, **152**, p 283-285
9. N.Y. Ayoub, C.C. Almasan, E.A. Early, J.T. Markert, C.L. Seaman, and M.B. Maple, The Effect of Indium Substitution for Copper on the Superconductivity of the Electron-Doped System Nd-Ce-Cu-O, *Physica C*, 1990, **170**, p 211-214
10. B. Shinozaki, S. Takada, N. Kokubo, K. Makise, K. Mitsuichi, K. Yamada, K. Yano, and H. Nakamura, Superconducting Characteristics and Microstructure of Polycrystalline Zn-Doped In_2O_3 Films, *Physica C*, 2011, **471**, p 717-720
11. T. Kijima, H. Sushida, T. Noguchi, M. Yada, and M. Machida, Synthesis and Characterisation of a New Layered Cuprate $In_2Ba_2CuO_{6-\delta}$, *J. Solid State Chem.*, 1997, **131**, p 177-180
12. R. Horyń, E. Bukowska, and A. Sikora, Studies of BaO-In_2O_3-CuO Ternary System. Part I: Phase Equilibria in the Isothermal Cross-Section of 930°C, *J. Alloy. Compd.*, 2000, **305**, p 103-108
13. O.V. Godzhieva, N.V. Porotnikov, and V.P. Pikhidchuk, Physical-Chemical Study of Triple Oxides Formed in In_2O_3-CaO-CuO System, *Zhur. Neorg. Khim.*, 1992, **37**, p 1184-1188
14. M. Marezio, Refinement of Crystal Structure of In_2O_3 at 2 Wavelengths, *Acta Crystallogr.*, 1996, **20**, p 723-728

15. J.K. Liang, C. Zhan, W. Fei, and S.S. Xie, Phase-Diagram of SrO-CaO-CuO Ternary-System, *Solid State Commun.*, 1990, **75**, p 247-252
16. A.S. Kosmynin, B.V. Slobodin, V.L. Balashov, I.K. Garkushin, A.A. Fotiev, and A.S. Trunin, Phase-Equilibria in the CaO-SrO-CuO System (≥70 mol% CuO), *Inorg. Mater.*, 1995, **7**, p 867-870
17. N.M. Hwang, R.S. Roth, and C.J. Rawn, Phase-Equilibria in the Systems SrO-CuO and SrO-1/2Bi_2O_3, *J. Am. Ceram. Soc.*, 1990, **73**, p 2531-2533
18. R.O. Suzuki, P. Bohac, and L.J. Gauckler, Thermodynamics and Phase-Equilibria in the Sr-Cu-O System, *J. Am. Ceram. Soc.*, 1992, **75**, p 2833-2842
19. M. Nevřiva and H. Kraus, Study of Phase-Equilibria in the Partially Open Sr-Cu-(O) System, *Physica C*, 1994, **235-240**, p 325-326
20. C.B. Alcock and B.Z. Li, Thermodynamic Study of the Cu-Sr-O System, *J. Am. Ceram. Soc.*, 1990, **73**, p 1176-1180
21. M.T. Weller and D.R. Lines, Structure and Oxidation-State Relationships in Ternary Copper Oxides, *J. Solid State Chem.*, 1989, **82**, p 21-29
22. E.M. McCarron, M.A. Subramanian, J.C. Calabrese, and R.L. Harlow, The Incommensurate Structure of $(Sr_{14-x}Ca_x)Cu_{24}O_{41}$ ($0 < x \sim 8$) a Superconductor By-Product, *Mater. Res. Bull.*, 1988, **23**, p 1355-1365
23. C.L. Teske and H. Müller-Buschbaum, Über Erdalkalimetall-Oxocuprate. Alkaline Earth Metal Oxocuprates. 4. $SrCu_2O_2$, *Z. Anorg. Allg. Chem.*, 1970, **379**, p 113-121
24. N. Kobayashi, Z. Hiroi, and M. Takano, Compounds and Phase Relations in the SrO-CaO-CuO System Under High Pressure, *J. Solid State Chem.*, 1997, **132**, p 274-283
25. H.-R. Freund and H. Müller-Buschbaum, Oxocuprates. 25. About $In_2Cu_2O_5$, *Z. Anorg. Allg. Chem.*, 1978, **441**, p 103-106
26. E.L. Belokoneva, L.I. Leonyuk, and N.I. Leonyuk, Single Crystal Growth and Crystal Structures of In_2CuO_4 $(Nd,Ce)_2CuO_4$ and of the Tetragonal Copper Deficient $Sm(Ba,Sm)_2Cu_{3-y}O_z$ Phase, *Svekhprovodimost*, 1991, **4**, p 563-569
27. Z. Li, J. Sun, L. You, H. Jiao, G. Li, X. Jing, F. Liao, and J. Lin, Phase Equilibrium of the In_2O_3-TiO_2-MO (M = Ca, Sr) Systems and the Structure of $In_6Ti_6CaO_{22}$, *Chem. Mater.*, 2005, **17**, p 2186-2192
28. R. von Schenk and H. Müller-Buschbaum, Alkaline-Earth Oxoindates. 3. Crystal-Structure Investigation on $SrIn_2O_4$, *Z. Anorg. Allg. Chem.*, 1973, **398**, p 24-30
29. R. von Schenk and H. Müller-Buschbaum, New Alkaline-Earth Metal Oxoindate-$Sr_2In_2O_5$, *Z. Anorg. Allg. Chem.*, 1973, **395**, p 280-286
30. T.J.B. Holland and S.A.T. Redfern, Unit Cell Refinement from Powder Diffraction Data: The Use of Regression Diagnostics, *Mineral. Mag.*, 1997, **61**, p 65-77
31. X. Li, C. Xia, X. He, X. Gao, S. Liang, G. Pei, and Y. Dong, Enhancement of Ferromagnetic Properties in $In_{1.99}Co_{0.01}O_3$ by Additional Cu Doping, *Scripta Mater.*, 2008, **58**, p 171-174
32. M. Sasaki, K. Yasui, S. Kohiki, H. Deguchi, S. Matsushima, M. Oku, and T. Shishido, Cu Doping Effect on Optical and Magnetic Properties of In_2O_3, *J. Alloy. Compd.*, 2002, **334**, p 205-210
33. J.-C. Grivel and N.H. Andersen, Subsolidus Phase Relations of the SrO-RE_2O_3-CuO Systems (RE = Tm, Lu and Sc), *J. Alloy. Compd.*, 2005, **391**, p 292-295
34. F. Wu, S. Xie, Z. Chen, and J. Ling, Subsolidus Phase Relations of the Y_2O_3-SrO-CuO System, *J. Mater. Sci.*, 1992, **27**, p 3082-3084
35. W. Wong-Ng, Q. Huang, I. Levin, J.A. Kaduk, J. Dillingham, T. Haugan, J. Suh, and L.P. Cook, Crystal Chemistry and Phase Equilibria of Selected SrO-R_2O_3-CuO_x and Related Systems; R = Lanthanides and Yttrium, *Int. J. Inorg. Mater.*, 2001, **3**, p 1283-1290
36. C.Q. Han, X.L. Chen, J.K. Liang, Q.L. Liu, Y. Chen, and G.H. Rao, The Ternary System Tm_2O_3-SrO-CuO: Compounds and Phase Relations, *J. Alloy. Compd.*, 2000, **309**, p 95-99
37. J.-C. Grivel and N.H. Andersen, Subsolidus Phase Relations of the SrO-Er_2O_3-CuO System, *J. Alloy. Compd.*, 2005, **389**, p 186-189
38. J.-C. Grivel and N.H. Andersen, Subsolidus Phase Relations of the SrO-REO_x-CuO Systems (RE = Ce, Pr and Tb), *J. Alloy. Compd.*, 2007, **436**, p 261-265
39. R.D. Shannon, Revised Effective Ionic-Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides, *Acta Crystallogr. A*, 1976, **32**, p 751-767